

# A Janus-type Heterogeneous Surfactant for Adipic Acid Synthesis

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A highly water-dispersible heterogeneous Brønsted acid surfactant was prepared by synthesis of a bi-functional anisotropic Janus-type material. The catalyst comprises ionic functionalities on one side and propyl-SO<sub>3</sub>H groups on the other. The novel material was investigated as a green substitute of a homogeneous acidic phase transfer catalyst (PTC). The activity of the catalyst was investigated for the aqueous-phase oxidation of cyclohexene to adipic acid with 30% hydrogen peroxide even in a decagram-scale. It can also be used for the synthesis of some other carboxylic acid derivatives as well as diethyl phthalate.

Since adipic acid is one of the building blocks for the production of nylon-6,6 by polycondensation with hexamethylene diamine, it is the industrially most important dicarboxylic acid.<sup>[1]</sup> In commercial processes adipic acid is mainly synthesized by the nitric acid oxidation of a mixture of cyclohexanol and cyclohexanone (so-called KA oil) with copper(II) and ammonium metavanadate as the catalysts.<sup>[1]</sup> The emission of stoichiometric amounts of nitrous oxide (N<sub>2</sub>O) as the by-product is surely a serious environmental disadvantage of this process. N<sub>2</sub>O is a greenhouse gas with a very long atmospheric lifetime and a

powerful heat trapping efficiency. Further negative environmental effects of N<sub>2</sub>O are related to its capability to destroy ozone in the atmosphere and its contribution to the acidification of rain.

Due to this, there is interest in using alternative, cheap and greener oxidizing reagents such as hydrogen peroxide. Due to new technologies for a safer and more efficient use of hydrogen peroxide in industry, the production of H<sub>2</sub>O<sub>2</sub> was increased while its price had decreased during the last decades.<sup>[2]</sup> The aqueous-phase oxidation of cyclohexene with hydrogen peroxide as the oxidizing agent and tungstate as the catalyst was introduced by Noyori and co-workers.<sup>[3]</sup> It opens up an economically and ecologically interesting alternative access to adipic acid. Further significant advantages of this reaction are the formation of water as the sole by-product, the relatively mild reaction conditions and the high selectivity. However, in order to obtain sufficient miscibility between the aqueous oxidizing agent and the organic substrate, the phase transfer catalyst (CH<sub>3</sub>(n-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N<sup>+</sup>HSO<sub>4</sub><sup>-</sup>) has to be used. It was shown that this PTC also promotes the activity of H<sub>2</sub>O<sub>2</sub> for the oxidation. However, the quaternary ammonium salt is expensive and not a safe reagent in terms of its environmental impact.

Based on the strategy implemented by Noyori, several other homogeneous and heterogeneous catalysts were developed for the oxidative cleavage of cyclohexene to adipic acid during the last years.<sup>[4]</sup> Although some valuable achievements could be realized, the reaction still requires further improvements especially in an environmental point of view. In particular, the removal of the PTC from the reaction mixture and its reuse has not been realized in a satisfying manner up to now. In contrast, a heterogeneous version in the form of a PTC or a surfactant is less corrosive, can be simply handled, stored and separated from the reaction mixture. The Janus strategy for the synthesis of anisotropic materials gives novel opportunities for the synthesis of a new generation of heterogeneous catalysts with comparable miscibility to homogeneous catalysis.

Janus-type materials are defined as solids possessing a chemically anisotropic surface. During the last years, they have attracted attention for their synthesis and applications in different fields<sup>[5]</sup> especially in catalysis.<sup>[6]</sup> A novel sub-group of these materials are anisotropically functionalized catalysts so-called Janus interphase catalysts. Very recently, we published a simple and practical procedure for the preparation of such Janus interphase catalysts.<sup>[7]</sup> In the present manuscript we report the synthesis of the first amphiphilic and water dispersible Janus interphase Brønsted acid catalyst and its application as a heterogeneous analogue of a PTC for the

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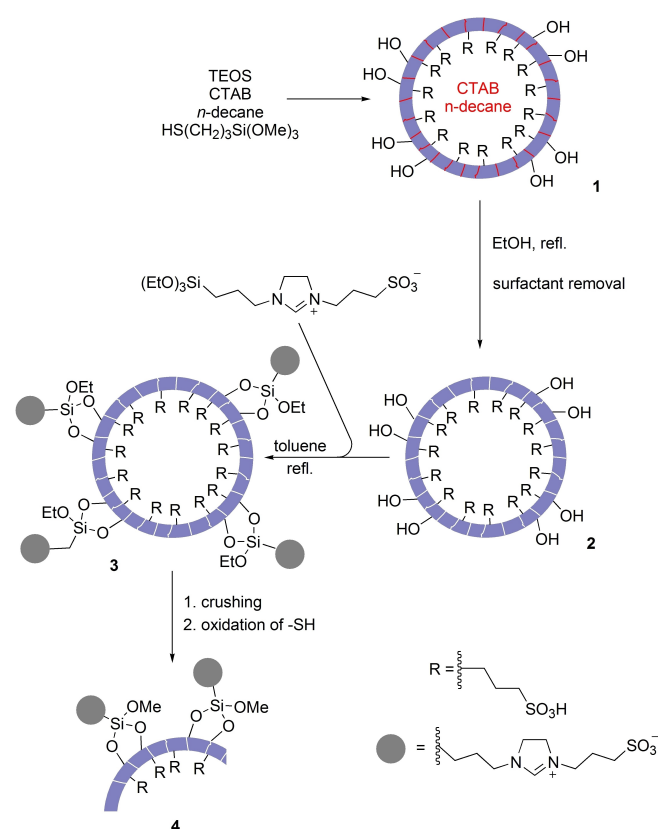
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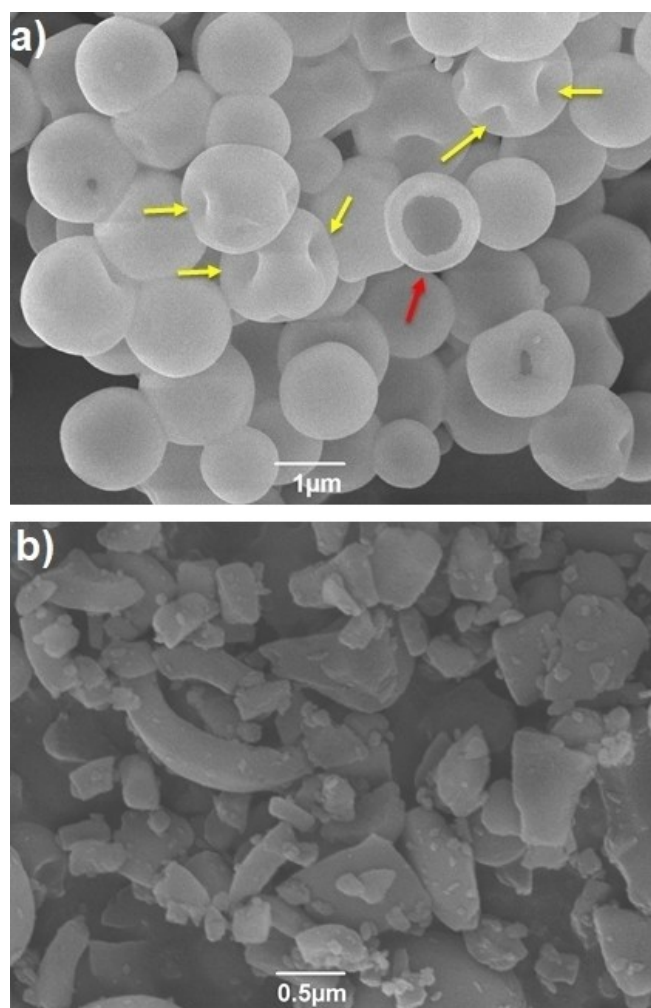
aqueous-phase oxidation of cyclohexene to adipic acid. The functionalization of the material's surface is highly compatible with both the aqueous oxidant and the organic substrate. In other words, the catalyst provides an optimal balance of hydrophobicity/hydrophilicity for an efficient emulsification of organic and aqueous phases. Consequently, the surfactant-like material can be used as a substitute for the established homogeneous acidic PTC. A schematic illustration of the material's preparation is shown in Scheme 1.

In the first step, porous hollow silica particles **1** bearing immobilized 3-mercaptopropyl groups on the inner surface were synthesized by applying a modified method for the preparation of Stöber silica particles.<sup>[8]</sup> After removing the surfactant (material **2**), zwitterionic groups were grafted on the outer surface of the hollow silica particles giving material **3**. Finally, the hollow spheres were crushed and the thiol groups were oxidized using 30% H<sub>2</sub>O<sub>2</sub>.<sup>[9]</sup> Details for the synthesis of catalyst **4** are described in the Supporting Information.

Elemental analysis (CHNS) of material **2** revealed that the loading of thiol groups is 0.65 mmol·g<sup>-1</sup>, while the loading of ionic functionalities in **4** was found to be 0.54 mmol·g<sup>-1</sup>. The morphology of the material before and after the crushing was explored by means of scanning electron microscopy (SEM, Figure 1). SEM images show sphere-like geometries for **3** with a rather uniform size of approx. 1 μm and some surface deformations (yellow arrows) coming from the intrinsic hollow structure. Moreover, a uniform wall thickness of the particles is



**Scheme 1.** Schematic synthesis of the water dispersible Janus surfactant.



**Figure 1.** SEM images of a) the hollow structures of **3**. The yellow arrows assign some deformations on the surface of the hollow silica spheres. A demonstration of the uniform wall thickness and the size of a hollow sphere is assigned by the red arrow. b) The curved/nanosheet structures of the final, crushed catalyst **4**.

clearly observable from a broken species (red arrow). The N<sub>2</sub> adsorption-desorption isotherms of materials **2** and **4** (Figure 1S, Supporting Information) show a type-IV profile, which is typical for mesoporous compounds. The calculated BET surface areas, the average pore diameter (BJH method) and the pore volume for the as-synthesized material **2** are 1021 m<sup>2</sup>/g, 2.24 nm and 0.57 mL/g while the according values for the final catalyst **4** are 530 m<sup>2</sup>/g, 2.6 nm and 0.34 mL/g, respectively.

The decrease of the specific surface area and of the pore volume from the freshly synthesized hollow silica spheres **2** to the final crushed catalyst **4** provides evidence for the successful functionalization of the surface. The specific surface area of the catalyst after two steps of functionalization is comparable to some other established mesoporous silica-based catalysts.<sup>[10]</sup>

All peaks in the <sup>13</sup>C CP-MAS NMR spectrum (Figure 2) of material **4** can be assigned to the carbon atoms of the introduced functional groups. Carbon atoms C1 and C12 are directly connected to silicon atoms and thus are highly shielded

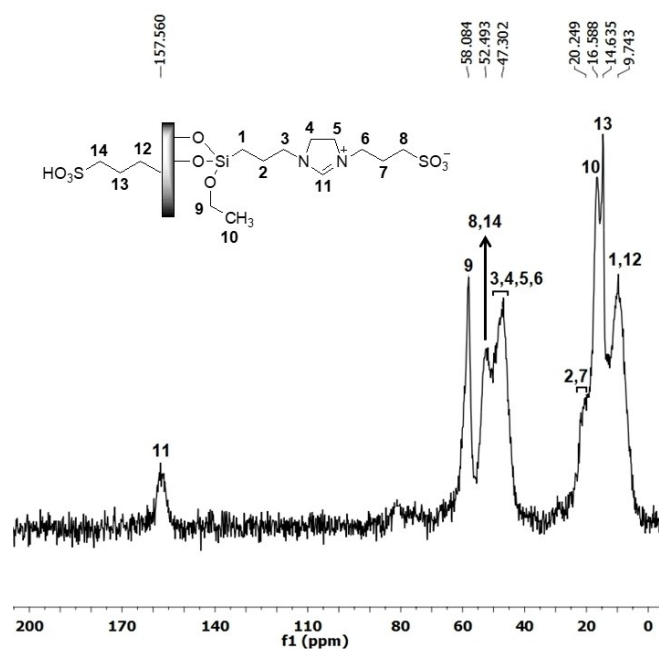


Figure 2. Solid-state  $^{13}\text{C}$  CP-MAS NMR spectra of 4.

leading to a broad resonance at around 9.7 ppm. Carbon atoms C10 and C13 can be identified as separated signals while carbon atoms C2 and C7 have rather identical chemical shifts and are observed as a shoulder at around 20.2 ppm. In addition, carbon atoms C3–C6 have almost identical chemical shifts and therefore are observed as one broad signal. The chemical shift of carbon atoms C8 and C14 that are directly connected to the  $-\text{SO}_3\text{H}$  resp.  $-\text{SO}_3^-$  groups is 52.5 ppm, the resonance of the  $\alpha$ -carbon atoms of some residual ethoxy groups coming from the grafted ionic precursor is observed at 58.1 ppm. The resonance of the unique  $\text{sp}^2$  hybridized carbon atom C11 is observed at 157.6 ppm.

The  $^{29}\text{Si}$  CP-MAS NMR spectrum of material 4 (see Figure 2S, Supporting Information) exhibits two dominant resonances at around  $-110$  and  $-120$  ppm, being attributed to  $\text{Q}^3$  [ $\text{Si}(\text{OSi})_3\text{OH}$ ] resp.  $\text{Q}^4$  [ $\text{Si}(\text{OSi})_4$ ] species in the framework of the materials. Two further resonances in this spectrum at around  $-68$  and  $-75$  ppm can be assigned to  $\text{T}^2$  [ $\text{RSi}(\text{OSi})_2(\text{OH})$ ] and  $\text{T}^3$  [ $\text{RSi}(\text{OSi})_3$ ] units and thus provide further evidence for the successful covalent immobilization of the triethoxysilane precursors on the surface of the materials.

To study the particle size distribution as well as particle dispersibility of catalyst 4 in water, laser diffraction analysis was employed (Figure 3). The analyses were repeated six times and the results indicate an excellent reproducibility of the measured data. In our previous report,<sup>[7]</sup> we investigated two different hydrophobic/hydrophilic catalysts by means of this analytic method. In these cases, the formation of some temporary agglomerations of Janus-type nanosheets in the solution was found, leading to particles with diameters of up to  $30\ \mu\text{m}$ . These agglomerated structures were proposed as the catalytically active regions in the emulsion. In the present case however, a

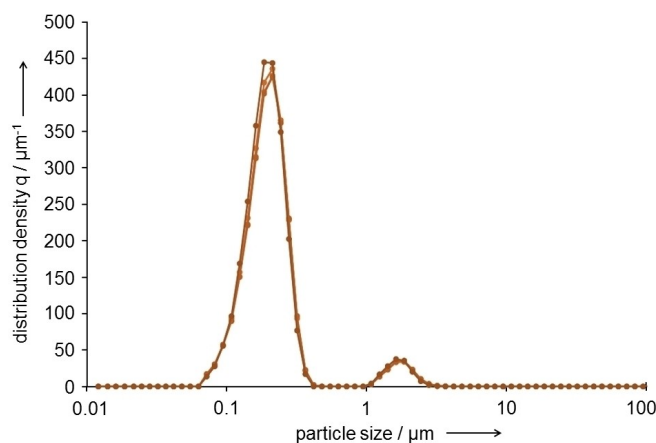
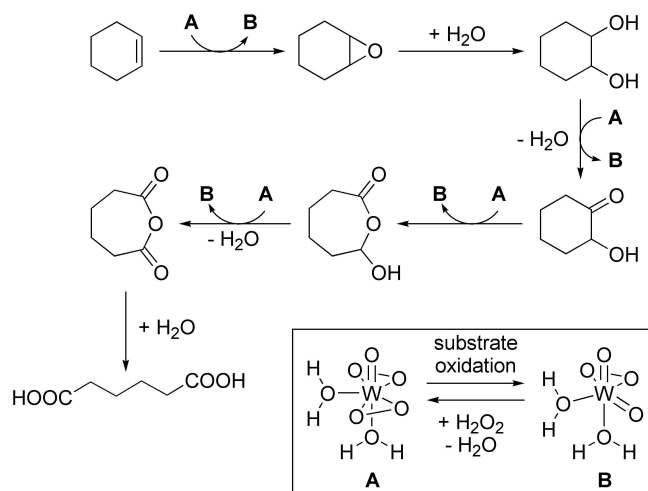


Figure 3. Laser diffraction particle size analysis summarized over six measurements of material 4 dispersed in water.

bimodal particle distribution with a major population having a particle size at around 240 nm and a minor population having a size around  $1.8\ \mu\text{m}$  (approx. the double size of the hollow spheres of material 3) were observed. This result suggests that unlike our previous report, most of the crushed particles of material 4 are completely dispersed in the aqueous medium without the formation of a significant amount of agglomerations.

The activity of the surfactant-like material 4 was investigated for the oxidative cleavage of cyclohexene to adipic acid. Scheme 2 presents the mechanism for this reaction as proposed by Noyori et al.<sup>[3]</sup> An in-situ generated peroxotungstate species converts cyclohexene to epoxycyclohexane, followed by a proton catalyzed ring opening of this intermediate to *trans*-1,2-cyclohexanediol in the acidic aqueous medium. The oxidation of one of the hydroxyl groups gives the corresponding  $\alpha$ -hydroxyketone, which is the substrate for a Baeyer-Villiger oxidation leading to a hydroxylactone. Finally, the remaining



Scheme 2. Stepwise oxidation of cyclohexene to adipic acid. The inset shows the action and regeneration of the catalyst.

hydroxyl group is oxidized to produce adipic anhydride, which is rapidly hydrolyzed in the presence of the acidic Janus-type catalyst **4**.

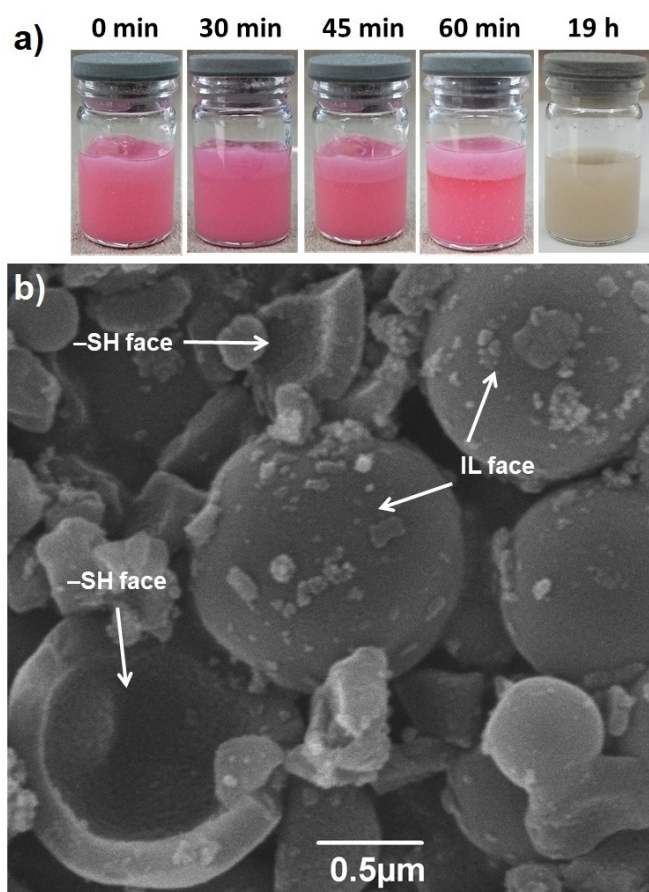
An image of the initial reaction mixture containing the catalyst, cyclohexene and aqueous  $\text{H}_2\text{O}_2$  is shown in Figure 4a. After shaking the suspension for 5 minutes, the color of the mixture turned to red in the presence methyl orange as pH indicator. Moreover, the phase boundary had disappeared and a uniform suspension had formed, which turned out to be stable for up to one hour under static conditions. This proves the excellent miscibility of organic and aqueous phases in the presence of the heterogeneous surfactant **4**. It is worth to be mentioned at this point that the homogeneity of the reaction mixture increased shortly after the reaction was started, which can be explained by the formation of more polar intermediates from the initially present, non-polar cyclohexene.

At the end of reaction, a completely uniform suspension was observed due to the interaction of the polar product with

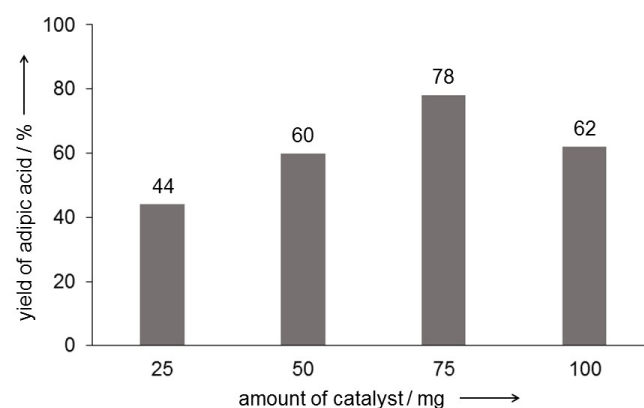
the anisotropic functionalities of the catalyst's faces (Figure 4a, right). To provide additional evidence for the selective functionalization of the material, negatively charged citrate-capped  $\text{Fe}_3\text{O}_4$  nanoparticles (citrate@ $\text{Fe}_3\text{O}_4$ ) were used according to a recently published process to label the ionic liquid face of catalyst.<sup>[6]</sup> To do this, material **3** was partially crushed to form large particles which are more suitable for the analysis by SEM than smaller ones. Then the material was labelled by mixing with citrate@ $\text{Fe}_3\text{O}_4$  before the oxidation of the  $-\text{SH}$  groups and the resulting solid was analyzed by SEM. The resulting image (Figure 4b) shows the high affinity of the outer (ionic liquid) face to the citrate@ $\text{Fe}_3\text{O}_4$  particles, while the inner  $-\text{SH}$  face almost remains untouched by the citrate@ $\text{Fe}_3\text{O}_4$  particles. This indicates that the two different groups are selectively bound to the inner resp. outer surface of the support.

According to Scheme 2, the reaction requires four equiv. of  $\text{H}_2\text{O}_2$ . To guarantee an almost complete conversion of cyclohexene, 4.4 equivalents of the oxidant were used.<sup>[3]</sup> It turned out to have a positive impact on the outcome of the reaction,<sup>[11]</sup> to heat the mixture first to  $71^\circ\text{C}$  (near to the boiling point of the initial reaction mixture) for 3 h. At the end of this step, cyclohexene was completely converted to cyclohexene oxide which has higher boiling point. Then, the temperature was raised to  $87^\circ\text{C}$  for 16 h. The dependence of the yield from the amount of material **4** in the mixture is depicted in Figure 5. Moderate yields of adipic acid are obtained with 25 and 50 mg of the **4**. However, in the presence of 75 mg of **4** overall 78% of pure adipic acid (after recrystallization) were formed. By further increasing the amount of surfactant **4** to 100 mg, the yield of adipic acid reached 62%. Such a decrease of yield can be explained by the increase of the ionic strength in the suspension in the presence of large amounts of the catalyst. This will slow down the diffusion of an organic substrate.

It was found that in the absence of catalyst, the oxidation of cyclohexene led to the formation of small amounts of adipic acid under the optimized conditions (less than 5%). Moreover, the yield of adipic acid reached only 8% when material **2**



**Figure 4.** a) Images of the reaction mixture for the oxidation of cyclohexene at different times (0 to 60 min) in the presence of two drops of an aqueous 0.1% molar methyl orange solution as a colour and pH indicator and an image of the final mixture in the absence of the indicator (right). Composition of the initial mixtures: 75 mg of catalyst **4**, 5 mmol (0.5 ml) of cyclohexene, 22 mmol (2.25 mL) of 30%  $\text{H}_2\text{O}_2$  and 17 mg (0.05 mmol) of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ . b) SEM image of the labelled material before the oxidation step of the thiol ( $-\text{SH}$ ) groups decorated with citrate@ $\text{Fe}_3\text{O}_4$  nanoparticles. The outer ionic liquid face is labelled with citrate@ $\text{Fe}_3\text{O}_4$  nanoparticle and the inner  $-\text{SH}$  face shows almost no interaction.



**Figure 5.** The influence of the amount of catalyst **4** on the outcome of the oxidation of cyclohexene to adipic acid. Reaction conditions: 5 mmol (0.5 ml) of cyclohexene, 22 mmol (2.25 mL) of 30% aqueous  $\text{H}_2\text{O}_2$  and 17 mg (0.05 mmol) of  $\text{Na}_2\text{WO}_4 \cdot (\text{H}_2\text{O})_2$ ,  $71^\circ\text{C}$  (3 h) then  $87^\circ\text{C}$  (16 h). Yields refer to isolated, pure adipic acid after recrystallization from ethyl acetate.

(75 mg) was used as the catalyst and the catalyst showed just a weak emulsifying character. Although material **3** showed better emulsifying properties compared to **2**, the yield of adipic acid did not exceed over 15%. We found that when the acidic site of catalyst **4** was neutralized with a 1% solution of sodium bicarbonate, the resulting material had a very good emulsifying performance. However, the oxidation of cyclohexene with this catalyst afforded just 10% of adipic acid. These observations suggest that the presence of acidic groups accompanied by amphiphilic nature of the material is crucial for achieving high catalytic activity.

In each reaction, the catalyst was simply separated by filtration or centrifugation from the reaction mixture. Regeneration of catalyst **4** is possible by drying the filtered solid under vacuum. The catalyst recovered this way was tested in two further batch reactions under the conditions shown in the caption of Figure 5 and afforded 76% resp. 70% of adipic acid for the second resp. the third run. Including the fact that there is some loss of solid material during the filtration process, surfactant **4** has preserved its activity over three runs.

Encouraged by the results obtained from the oxidation of cyclohexene to adipic acid, we investigated the application of material **4** for further oxidation reactions in the following (Table 1). The oxidation of *trans*-1,2-cyclohexanediol furnished with an almost identical yield of adipic acid as the oxidation of cyclohexene (entry 2). Cyclohexanone and cyclohexanol can also be converted to adipic acid with high yield (entries 3 and 4) which is in general fitting to the mechanistic image given in Scheme 2. Aside to adipic acid, glutaric acid is another important building block for polymer synthesis. By using material **4** and sodium tungstate, glutaric acid can be prepared by the oxidation of cyclopentene. Due to the low boiling point of this substrate (44–46 °C), the mixture was heated only to 45 °C in the first step (entry 5). When styrene was used as the substrate, high yields of benzoic acid were obtained (entry 6). The according C1 product generated by the cleavage of the C=C double bond of styrene was not analyzed in detail. Moreover, material **4** was tested for the ring opening of the phthalic anhydride in water (entry 7) since an acid-catalyzed ring opening was postulated to occur during the formation of adipic acid. Here, excellent yields of phthalic acid demonstrate that the ring-opening step in the depicted mechanism (Scheme 2) is indeed a rapid reaction. The acidity of the catalyst was further investigated for the synthesis diethyl phthalate

being an important plasticizer used in industries. The reaction proceeded well with up to 85% yield of diethyl phthalate (entry 8).

To understand the mode of action of surfactant **4**, it helps to recall the mechanistic discussions on this reaction that have been published in the past. It is not yet completely clear, which step of the described reaction sequence in Scheme 2 is the rate-determining one. The olefin epoxidation should be rapid with the given tungsten catalyst. The same is true for the ring-opening of the epoxide in the presence of the Brønsted acidic material **4** as shown above. Thomas et al. found that in the following step the *trans*-diol isomer reacts significantly slower than the *cis*-diol.<sup>[12]</sup> Therefore, improvement of the *trans*-diol oxidation step is expected to affect the overall reaction rate. However, when we used the *trans*-diol instead of the cyclohexene as starting material, no noticeable changes in the yield of adipic acid was found. This observation explains the independence of the reaction rate from the epoxidation of cyclohexene. In the synthesis of adipic acid by oxidation of cyclohexanol and cyclohexanone, Sato et al. proposed that the Baeyer-Villiger oxidation might be the rate-determining step of the reaction.<sup>[13]</sup> A low reaction rate of the Baeyer-Villiger oxidation of  $\alpha$ -hydroxyketones was also proposed by Noyori et al.<sup>[3a]</sup>

To find evidence for these suggestions, we set up two experiments considering the oxidation of cyclohexanone and cyclohexanol according to the conditions employed in entries 3 and 4 of Table 1. The reactions were quenched after 8 h, then the mixtures were analyzed by means of gas chromatography. In case cyclohexanone was used as the starting material the conversion was not quantitative, some cyclohexanone was still present in the mixture. On the other hand, in the same reaction time, the oxidation of cyclohexanol led to complete conversion of the starting material. However, again the presence of some cyclohexanone (from the oxidation of cyclohexanol) was observed. These findings make plausible that the Baeyer-Villiger oxidation of the ketone is the rate-determining step.

As a working hypothesis to explain the high efficiency of material **4**, we believe that the rapid epoxide formation and hydrolysis generates large amounts of the intermediate 1,2-diol that can strongly interfere with the functional groups on the surface of the material. The same is true for all other intermediates, hydrogen peroxide and tungsten species. It might be that highly polar water is partially expelled from the

**Table 1.** Investigation of the catalytic activity of material **4**.

Entry	Substrate(s)	Time [h]/Temp. [°C]	H <sub>2</sub> O <sub>2</sub> [equiv.]	Product	Isolated yield[%] <sup>[a]</sup>
1	cyclohexene	3/71 then 16/87	4.4	adipic acid	78
2	<i>trans</i> -1,2-cyclohexanediol	16/87	3.3	adipic acid	79
3	cyclohexanone	16/87	3.3	adipic acid	83
4	cyclohexanol	16/87	4.4	adipic acid	80
5	cyclopentene	3/45 then 16/87	4.4	glutaric acid	76
6	styrene	16/87	4.4	benzoic acid	84
7	phthalic anhydride	16/70	–	phthalic acid	98 <sup>[b,c]</sup>
8	phthalic anhydride + ethanol	16/70	–	diethyl phthalate	85 <sup>[b,d]</sup>

[a] Reaction conditions: 5 mmol of substrate, 75 mg of material **4**, 17 mg of Na<sub>2</sub>WO<sub>4</sub>·(H<sub>2</sub>O)<sub>2</sub>, unless otherwise stated. [b] The reactions were performed in the absence of the oxidant and sodium tungstate. [c] 2 mL of H<sub>2</sub>O were used for the hydrolysis reaction. [d] 2 mL of ethanol were used.

surface,<sup>[14]</sup> which despite all polar groups still has some organic character. This would in addition increase the local concentrations of all other players at the surface. The final product adipic acid is the most polar organic compound in the reaction sequence. It therefore should be better soluble in the aqueous phase and leave the surface.

Since adipic acid synthesis is an industrially important process, the possibility for a process scale-up is of interest. Only a few examples for applications of Janus-type materials in catalytic large-scale syntheses have been reported so far.<sup>[15]</sup> Therefore a protocol was worked out wherein the amounts of all reaction partners were increased by a factor of 30 (e.g. 12.3 g resp. 150 mmol of cyclohexene). At the end of this reaction, the catalyst was separated from the hot slurry by filtration. The flask containing the filtrate was immersed into an ice bath for 30 min and the precipitated adipic acid was separated by filtration. After washing with cold water to remove residual H<sub>2</sub>O<sub>2</sub> and tungsten(VI) species and drying at room temp. 17.8 g (81 %) of pure adipic acid could be obtained.

To conclude, by mimicking the properties of a homogeneous Brønsted acidic PTC, the heterogeneous surfactant **4** was prepared. In combination with Na<sub>2</sub>WO<sub>4</sub>·(H<sub>2</sub>O)<sub>2</sub> it turned out to give a highly active mixture for the selective oxidation of cyclohexene to adipic acid. In addition, some other substrates can efficiently be oxidized such as cyclopentene, cyclohexanol, cyclohexanone and *trans*-1,2-cyclohexanediol). A scale-up resulting in the formation of almost 18 g of adipic acid was realized without further optimization of the reaction conditions. Catalyst regeneration is possible by simple filtration of **4**. The catalyst was tested in three consecutive batches without significant loss of reactivity. The complete and simple recovery of a highly active solid surfactant is a substantial step towards greener protocols and therefore of general importance for chemical synthesis and catalysis.

## Experimental Section

The details of experimental procedure for the synthesis of the catalyst and oxidation of cyclohexene are provided in the electronic supporting information.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** heterogeneous surfactant · Janus interphase catalyst · miscibility · aqueous-phase oxidation · adipic acid

- [1] a) R. A. Mayer in *The 100 most important chemical compounds*, 1<sup>st</sup> ed, Greenwood Press, London, 2007, pp. 20–23; b) M. T. Musser in *Ullmann's encyclopedia of industrial chemistry*, Wiley-VCH, Weinheim, 2005; c) S. Van de Vyver, Y. Román-Leshkov, *Catal. Sci. Technol.* 2013, 3, 1465–1479.
- [2] F. Cavani J H Teles, *ChemSusChem* 2009, 2, 508–534.
- [3] a) K. Sato, M. Aoki, R. Noyori, *Science* 1998, 281, 1646–1647; b) R. Noyori, M. Aoki, K. Sato, *Chem. Commun.* 2003, 1977–1986.
- [4] a) W. Zhu, H. Li, X. He, Q. Zhang, H. Shu, Y. Yan, *Catal. Commun.* 2008, 9, 551–555; b) Y. Wen, X. Wang, H. Wei, B. Li, P. Jin, L. Li, *Green Chem.* 2012, 14, 2868–2875; c) M. Vafaezadeh, M. M. Hashemi, *RSC Adv.* 2015, 5, 31298–31302; d) M. Vafaezadeh, M. M. Hashemi, *Chem. Eng. J.* 2013, 221, 254–257; e) Z. Saedi, S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, *Catal. Commun.* 2012, 17, 18–22; f) M. N. Timofeeva, O. A. Kholdeeva, S. H. Jhung, J.-S. Chang, *Appl. Catal. A* 2008, 345, 195–200; g) G. Lapisardi, F. Chiker, F. Launay, J.-P. Nogier, J.-L. Bonardet, *Catal. Commun.* 2004, 5, 277–281; h) Y. Deng, Z. Ma, K. Wang, J. Chen, *Green Chem.* 1999, 1, 275–276; i) M. Vafaezadeh, M. M. Hashemi, M. Shakourian-Fard, *Catal. Commun.* 2012, 26, 54–57; j) M. Vafaezadeh, M. M. Hashemi, *Catal. Commun.* 2014, 43, 169–172; k) M. Damm, B. Gutmann, C. O. Kappe, *ChemSusChem* 2013, 6, 978–982; l) C.-Y. Cheng, K.-J. Lin, M. R. Prasad, S.-J. Fu, S.-Y. Chang, S.-G. Shyu, H.-S. Sheu, C.-H. Chen, C.-H. Chuang, M.-T. Lin, *Catal. Commun.* 2007, 8, 1060–1064; m) B. C. Ranu, S. Bhadra, L. Adak, *Tetrahedron Lett.* 2008, 49, 2588–2591; n) Z. Bohström, I. Rico-Lattes, K. Holmberg, *Green Chem.* 2010, 12, 1861–1869.
- [5] a) A. Walther, A. H. E. Müller, *Chem. Rev.* 2013, 113, 5194–5261; b) M. Lattuada, T. A. Hatton, *Nano Today* 2011, 6, 286–308; c) J. Hu, S. Zhou, Y. Sun, X. Fang, L. Wu, *Chem. Soc. Rev.* 2012, 41, 4356–4378; d) Y. Song, S. Chen, *Chem. Asian J.* 2014, 9, 418–430; e) A. Walther, A. H. E. Müller, *Soft Matter* 2008, 4, 663–668; f) E. Poggi, J.-F. Gohy, *Colloid Polym. Sci.* 2017, 295, 2083–2108; g) F. Liang, C. Zhang, Z. Yang, *Adv. Mater.* 2014, 26, 6944–6949; h) F. Liang, B. Liu, Z. Cao, Z. Yang, *Langmuir* 2018, 34, 4123–4131; i) Z. Teng, X. Su, Y. Zheng, J. Sun, G. Chen, C. Tian, J. Wang, H. Li, Y. Zhao, G. Lu, *Chem. Mater.* 2013, 25, 98–105; j) Y. Chen, F. Liang, H. Yang, C. Zhang, Q. Wang, X. Qu, J. Li, Y. Cai, D. Qiu, Z. Yang, *Macromolecules* 2012, 45, 1460–1467; k) F. Liang, J. Liu, C. Zhang, X. Qu, J. Li, Z. Yang, *Chem. Commun.* 2011, 47, 1231–1233; l) X. Ji, Q. Zhang, F. Liang, Q. Chen, X. Qu, C. Zhang, Q. Wang, J. Li, X. Song, Z. Yang, *Chem. Commun.* 2014, 50, 5706–5709; m) F. Liang, K. Shen, X. Qu, C. Zhang, Q. Wang, J. Li, J. Liu, Z. Yang, *Angew. Chem. Int. Ed.* 2011, 50, 2379–2382.
- [6] a) Z. Wu, L. Li, T. Liao, X. Chen, W. Jiang, W. Luo, J. Yang, Z. Sun, *Nano Today* 2018, 22, 62–82; b) D. J. Cole-Hamilton, *Science* 2010, 327, 41–42; c) S. Crossley, J. Faria, M. Shen, D. E. Resasco, *Science* 2010, 327, 68–72; d) R. A. Pavlick, S. Sengupta, T. McFadden, H. Zhang, A. Sen, *Angew. Chem. Int. Ed.* 2011, 50, 9374–9377; e) L. Xia, H. Zhang, Z. Wei, Y. Jiang, L. Zhang, J. Zhao, J. Zhang, L. Dong, E. Li, L. Ruhlmann, Q. Zhang, *Chem. Eur. J.* 2017, 23, 1920–1929; f) X. Kong, C. Wu, L. Feng, J. Qu, P. Liu, X. Wang, X. Zhang, *Chem. Commun.* 2017, 53, 8054–8057; g) M. Zhang, Z. Tang, W. Fu, W. Wang, R. Tan, D. Yin, *Chem. Commun.* 2019, 55, 592–595; h) S. Cobo, J. Heidkamp, P. Jacques, J. Fize, V. Fourmond, L. Guetaz, B. Jousselme, V. Ivanova, H. Dau, S. Palacin, M. Fontecave, V. Artero, *Nat. Mater.* 2012, 11, 802–807; i) Z. Xue, H. Su, Q. Yu, B. Zhang, H. Wang, X. Li, J. Chen, *Adv. Energy Mater.* 2017, 7, 1602355–1602361; j) X. Wang, B. Guan, Y. He, Y. Zhang, Y. Cao, Y. Liu, Z. Qiao, Q. Huo, *ChemNanoMat* 2015, 1, 562–566; k) L. Xia, H. Zhang, Z. Wei, Y. Jiang, L. Zhang, J. Zhao, J. Zhang, L. Dong, E. Li, L. Ruhlmann, Q. Zhang, *Chem. Eur. J.* 2017, 23, 1920–1929; l) X. Ji, Q. Zhang, X. Qu, Q. Wang, X. Song, F. Liang, Z. Yang, *RSC Adv.* 2015, 5, 21877–21880; m) S. Yan, H. Zou, S. Chen, N. Xue, H. Yang, *Chem. Commun.* 2018, 54, 10455–10458; n) W. Gao, A. Pei, R. Dong, J. Wang, *J. Am. Chem. Soc.* 2014, 136, 2276–2279; o) R. A. Pavlick, S. Sengupta, T. McFadden, H. Zhang, A. Sen, *Angew. Chem. Int. Ed.* 2011, 50, 9374–9377; *Angew. Chem.* 2011, 123, 9546–9549.
- [7] M. Vafaezadeh, P. Breuninger, P. Löscher, C. Wilhelm, S. Ernst, S. Antonyuk, W. R. Thiel, *ChemCatChem* 2019, 11, 2304–2312.
- [8] W. Stöber, A. Fink, E. Bohn, *J. Coll. Interf. Sci.* 1968, 26, 62–69.
- [9] B. Schäfer, O. D. Malter, E. Kaigarula, A. Schübler, S. Ernst, W. R. Thiel, *Microporous Mesoporous Mater.* 2017, 251, 122–128.
- [10] a) L. Wang, A. Reis, A. Seifert, T. Philippi, S. Ernst, M. Jia, W. R. Thiel, *Dalton Trans.* 2009, 3315–3320; b) L. Wang, S. Shylesh, D. Dehe, T.

- Philippi, G. Dörr, A. Seifert, Z. Zhou, M. Hartmann, R. N. K. Taylor, M. Jia, S. Ernst, W. R. Thiel, *ChemCatChem* **2012**, *4*, 395–400; c) S. Farsadpour, L. T. Ghoochany, S. Shylesh, G. Dörr, A. Seifert, S. Ernst, W. R. Thiel, *ChemCatChem* **2012**, *4*, 401–407.
- [11] P. Jin, Z. Zhao, Z. Dai, D. Wei, M. Tang, X. Wang, *Catal. Today* **2011**, *175*, 619–624.
- [12] S. Lee, R. Raja, K. D. M. Harris, J. M. Thomas, B. F. G. Johnson, G. Sankar, *Angew. Chem. Int. Ed.* **2003**, *42*, 1520–1523.
- [13] Y. Usui, K. Sato, *Green Chem.* **2003**, *5*, 373–375.
- [14] B. Karimi, M. Vafaezadeh, *RSC Adv.* **2013**, *3*, 23207–23211.
- [15] a) C. Tang, C. Zhang, J. Liu, X. Qu, J. Li, Z. Yang, *Macromolecules* **2010**, *43*, 5114–5120; b) C. Zhang, B. Liu, C. Tang, J. Liu, X. Qu, J. Li, Z. Yang, *Chem. Commun.* **2010**, *46*, 4610–4612.

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